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Abstract

An ambient pressure method for drying sol-gel materials has been used to synthesize highly porous vanadium oxide and molybdenum oxide materials with aerogel-like properties. The resulting solids exhibit 80 -90% porosity and high surface area (150 - 280 m^2/g). The synthesis approach uses liquid exchange to replace the pore fluid with a low surface tension, nonpolar solvent which reduces the capillary pressures developed during drying. The technique is adaptable to the preparation of porous thin films.

Keywords

A. microporous materials, A. oxides, B. sol-gel chemistry, D. microstructure

1. Introduction

Aerogels are highly porous nanostructured materials usually prepared by sol-gel processing followed by supercritical drying. The low density and nanoscale porosity of these materials lead to novel thermal, mechanical and optical properties so that aerogels have been widely investigated for such applications as thermal insulation, catalysts and catalyst supports, acoustics and gas filters.(1-3) In recent years it has become evident that the high surface area, porous morphology of aerogels is of interest for electrochemical applications including supercapacitors (4) and reversible cathode materials for lithium batteries (5, 6). Currently, silica aerogels are generating considerable interest because their highly porous nature produces the extremely low dielectric constant materials desired for microelectronics.(7)

The processing of aerogels by supercritical drying remains the most widely used approach for preparing these materials. This has imposed certain limitations to large scale commercialization because of the economics as well as potential hazards involved in bringing solvents to supercritical conditions. Moreover, supercritical extraction processes are inconvenient for preparing aerogel thin films which are of interest for electrochemical and microelectronics applications. Ambient pressure methods for preparing aerogel materials are just emerging and approaches for preparing silica have recently been reported.(8-15) The present paper extends the prior work reported for silica and establishes that relatively simple ambient pressure drying approaches can be adapted to sol-gel derived transition metal oxides. A closely related issue examined in this paper is how the properties of the solid-liquid interface may lead to high capillary pressures within a drying gel.

The highly porous, high surface area morphology of aerogels is accomplished by avoiding the densification (or shrinkage) which occurs when a wet gel network collapses from the capillary pressures generated during ambient drying. The amount of shrinkage

during drying is determined by two principal factors: the capillary pressure of the pore fluid and the stiffness of the inorganic gel network.(10) To prevent capillary forces from developing, supercritical drying is employed and the final dried aerogel exhibits minimal shrinkage upon drying, preserving the highly porous nanostructure of the wet gel. Ambient pressure gel shrinkage models have recently appeared in the literature.(16-18)

The ambient pressure drying methods which are based on minimizing the shrinkage of silicate gel systems either use chemical modification to alter condensation reactions (8-10) or strengthen the gel so that it may withstand capillary forces (11-14). Silica aerogel films were prepared using organic surface treatments in which terminal hydroxyl groups were replaced by nonreactive organosilicon groups via silylation. The purpose is to allow collapsing pores to "spring-back" instead of being closed permanently via condensation reactions. These films exhibit porosities of up to 98.5%.(8,9) Similarly, silica monoliths were prepared by methylating the surface of the pores prior to ambient pressure drying.(10) The use of network strengthening is achieved by using washing and aging treatments which coarsen the gel network and increase its resistance to collapse by the capillary forces generated during ambient pressure drying. Densities as low as $0.22 g/cm^3$ with specific surface areas of approximately 700 m^2/g have been reported. The benefits of using solvents with low surface tension were also noted in this study.(14) An earlier paper reported the curing of aged gels in alkyl alcohols and alkoxysilanes.(15) Low density silica materials (0.3-0.4 g/cm^3 and 600 m^2/g) were obtained by ambient pressure drying, but the authors did not consider the means by which these properties were obtained.

The present paper uses neither the surface modification nor the strengthening approaches developed for silica systems. The experimental work is based entirely on the use of low surface tension solvents to obtain high porosity, high surface area materials and represents the first report of synthesizing ambient pressure, aerogel-like materials of vanadium oxide and molybdenum oxide. The approach is compatible with the preparation of thin films.

2. Experimental

Vanadium oxide and molybdenum oxide (nominally V_2O_5 and MoO_3, respectively) wet gels were prepared from alkoxide precursors by previously developed sol-gel routes.(19,20) Vanadium oxide sols were prepared by adding a water/acetone solution to vanadyl-triisopropoxide (1:40:20 alkoxide:water:acetone). Gelation occurred in less than 5 sec. at 0°C. Molybdenum oxide sols were prepared by adding an acetonitrile, nitric acid, and water mixture (15:1:10:1 acetonitrile:nitric acid:water:Mo) with a 1:1 mixture of molybdenum(V)-isopropoxide and molybdenum(V)-trichloroisopropoxide. Gelation occurred in approximately two weeks at room temperature. The wet gel porosities were approximately 95% in both cases. After aging the wet gels 1-2 weeks, any residual water, alcohols, and unreacted precursors within the pores were removed by three washings in acetone of one day per wash.

The aged and acetone washed gels were then solvent-exchanged prior to ambient pressure drying. The acetone in the gels was exchanged with the desired low-surface tension alkane for three additional washings of one day each. The solvent-exchanged gels were then dried at room temperature under ambient pressure in flowing argon. Additional samples were prepared by drying gels directly from acetone, and also by supercritical CO_2 extraction. Residual solvent was removed by drying the gels in a vacuum oven at 150°C and 760 torr vacuum for 24 hours. BET analysis (Micromeritics ASAP 2010) was used to measure the specific surface area and pore size distributions were calculated from adsorption isotherm data of the dry gels. Bulk densities were measured using mercury pycnometry.

3. Results and Discussion

Ambient pressure drying of vanadium oxide and molybdenum oxide resulted in monolithic gels exhibiting aerogel-like surface areas with densities between those of aerogels and xerogels. The surface area and fraction porosity data are summarized in

Table 1. The data for the supercritically dried aerogels and for the acetone dried gels are included for comparison. The latter exhibit properties representative of xerogels. These data show that by employing low surface tension alkanes as drying liquids, low density vanadium oxide and molybdenum oxide gels may be obtained with aerogel-like surface areas in the range of 150-280 m^2/g. Porosity values of these high surface area gels are 80-90%, intermediate between those of acetone dried xerogels and supercritically dried aerogels.

TABLE 1.
Surface area and porosity data for vanadium oxide and molybdenum oxide gels dried under ambient pressure conditions and by supercritical methods.

Drying Liquid (21) (surface tension in mJ/m^2)	V_2O_5		MoO_3	
	surface area (m^2/g)	porosity (%)	surface area (m^2/g)	porosity (%)
acetone (23)	< 10	34	< 10	58
cyclohexane (25)	155	84	250	78
heptane (20)	200	86	---	---
hexane (18)	165	89	---	---
pentane (15)	185	89	280	84
supercritical CO_2	280	98	180	96

The BET isotherm data shown in Fig. 1 illustrate the behavior of vanadium oxide gels dried from the mother liquor of acetone/water, pentane, and supercritical CO_2. The virtual absence of gas adsorption for the acetone-dried material is typical of low surface area xerogels. The gradual increase in adsorption with increasing pressure for the supercritically dried aerogel indicates that it has a wide distribution of pore sizes (20 to 1000 Å). The aerogel dried from pentane exhibits less gas adsorption at lower pressures (i.e. smaller pore sizes), but has much higher adsorption at higher pressures. This result indicates that the pentane-dried gel has mostly large pores (500-1500 Å). The measurements also indicate that the BET surface area of vanadium oxide is less than the supercritically dried material whereas that of molybdenum oxide is actually greater. The cause of this behavior is not clear but should become better understood as TEM studies on aerogel morphology are completed.

An interesting point to note is that the characteristics of gels dried from acetone are dramatically different that those dried from cyclohexane. This occurs despite the fact that the surface tensions of the drying liquids are nearly the same and the wet gels within each oxide system were prepared under identical conditions. These data suggest that the capillary pressures induced in these gels are driven by factors other than the surface tension of the pore liquid. To explore this effect, the interfacial tensions were investigated in greater detail using the Good-Girifalco interaction parameter, Φ_G. This parameter accounts for the various van der Waal interaction forces occurring at the solid-liquid interface which can then be incorporated in calculations of capillary pressure.(22-26)

The interaction parameter, Φ_G, is defined in Equation 1 and related to the reversible work of adhesion, W^A (Equation 2), where α is electronic polarizability, I is the ionization potential, μ is the electronic dipole moment, k is the Boltzmann constant, T is temperature, γ is surface tension, subscripts L and S refer to the liquid and solid phases, respectively, and θ is the contact angle.(25,26) Equation (2) may be equated with the Young-Dupré relation for W^A (Equation 3) enabling $\cos\theta$ to be solved in terms of Φ_G.

$$\Phi_G = \frac{\frac{3}{2}\alpha_L\alpha_S\frac{I_L I_S}{I_L + I_S} + \frac{\alpha_L\mu_L^2 + \alpha_S\mu_S^2}{2} + \frac{\mu_L^2\mu_S^2}{3kT}}{\left(\frac{3}{4}\alpha_L^2 I_L + \alpha_L\mu_L^2 + \frac{\mu_L^4}{3kT}\right)^{0.5}\left(\frac{3}{4}\alpha_S^2 I_S + \alpha_S\mu_S^2 + \frac{\mu_S^4}{3kT}\right)^{0.5}} \qquad (1)$$

$$W^A = 2\Phi_G\left(\gamma_S\gamma_L\right)^{0.5} \qquad (2)$$

$$W^A = \gamma_L(1+\cos\theta) \qquad (3)$$

This expression for $\cos\theta$ is then substituted into the well-known cylindrical pore model (Equation 4) for capillary pressure, P_C, where d is the hydraulic pore diameter.(27) The

resulting equation for P_C (Equation 5) is used to approximate the relative magnitudes of induced capillary pressures as a function of the previously mentioned physical parameters of the drying liquid.

$$P_C = \frac{4\gamma_L \cos\theta}{d} \tag{4}$$

$$P_C = \frac{8\Phi_G(\gamma_L\gamma_S)^{0.5} - 4\gamma_L}{d} \tag{5}$$

The corresponding experimental work was carried out using a set of silica samples which were dried under the same conditions described for the vanadium oxide and molybdenum oxide samples. Silica was chosen as a model system for this calculation because it is a well known oxide system and the physical parameters required for calculating Φ_G are readily available. The silica gels were prepared using acid catalyzed tetramethoxysilane mixed with methanol and pH 5 buffer.(28)

Table 2 lists the surface areas and porosities measured for silica gels dried using the same liquids as those for the vanadium oxide and molybdenum oxide materials. The behavior of the silica system is similar to the transition metal oxides in that the acetone-dried gels possess a lower surface area and lower porosity than the corresponding gels dried in cyclohexane or the other nonpolar solvents. It is evident that the experimental data correlate with the calculated values of Φ_G. The systems exhibiting higher surface areas (1000 m^2/g) and greater porosities (70%) give Φ_G values of ~0.3 while the acetone dried material has a $\Phi_G = 0.9$. As shown in Equation 5, the capillary pressure scales with Φ_G and the values calculated for P_C (Table 2) are well within the range of pressures calculated for alkoxide gels with a range of densities, surface areas and contact angles.(27)

TABLE 2.
Surface area and porosity data for silica gels dried under ambient pressure conditions and by supercritical methods. Also included are calculated values for the Good-Girifalco interaction parameter, Φ_G, and the capillary pressure, P_C, in the drying gel.

Drying Liquid (21) (surface tension in mJ/m^2)	SiO_2			
	surface area (m^2/g)	porosity (%)	Φ_G	P_C (MPa)
acetone (23)	555	43	0.90	78
n-butanol (25)	685	50	0.53	44
cyclohexane (25)	1000	68	0.32	23
heptane (20)	1040	69	0.31	21
hexane (18)	1025	69	0.31	20
pentane (15)	1000	69	0.31	19
supercritical CO_2	1050	86		

This result indicates that surface tension is not the only factor to be considered when selecting drying liquids for ambient pressure processing of aerogel-like materials. The Good-Girifalco analysis shows that the solid-liquid interface also contributes to Φ_G and thus leads to increased capillary pressure. For this reason, oxide gels with relatively polar surfaces (e.g., SiO_2) exhibit higher surface areas and lower densities when dried using nonpolar drying liquids.

4. Conclusions

The use of low surface tension, nonpolar solvents as the pore fluid enables aerogel-like materials of vanadium oxide and molybdenum oxide to be prepared by ambient pressure drying. Capillary pressures generated during drying can be reduced by the selection of a drying liquid with low surface tension as well as minimal van der Waals interactions with the solid network. This liquid-exchange approach to producing aerogel materials is attractive because of its simplicity, the elimination of autoclave use, and its adaptability to thin film preparation.

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References

1. J. Fricke, Aerogels, Springer-Verlag, Berlin (1986).
2. R.J. Ayen and P.A. Iacobucci, Reviews in Chemical Engineering 5, 157 (1988).
3. M. Schneider and A. Baiker, Catal. Rev.-Sci. Eng. 37, 515 (1995).
4. S.T. Mayer, R.W. Pekala and J.L. Kaschmitter, J. Electrochem. Soc. 140, 446 (1993).
5. K. Salloux, F. Chaput, H.P. Wong and B. Dunn, J. Electrochem. Soc. 142, L191 (1995).
6. H.-K. Park, W.H. Smyrl and M.D. Ward, J. Electrochem. Soc. 142, 1068 (1994).
7. D.M. Smith, J. Anderson, C.C. Cho, G.P. Johnston and S.P. Jeng, Mat. Res. Soc. Symp. Proc. 381, 261 (1995).
8. S.S. Prakash, C.J. Brinker and A.J. Hurd, J. Non-Cryst. Solids 190, 264 (1995).
9. S.S. Prakash, C.J. Brinker, A.J. Hurd and S. M. Rao, Nature 374, 439 (1995).
10. D.M. Smith, D. Stein, J.M. Anderson, W. Ackerman, J. Non-Cryst. Solids 186, 104 (1995)
11. M.-A. Einarsrud, L.E. Farbrodt, S. Hæreid and V. Wittwer, Proc. SPIE 1727, 352 (1992).
12. M.-A. Einarsrud, S. Hæreid and V. Wittwer, Solar Energy Materials and Solar Cells, 31, 341 (1993)
13. S. Hæreid, M. Dahle, S. Lima and M.-A. Einarsrud, J. Non-Cryst. Solids 186, 96 (1995).
14. S. Hæreid, E. Nilsen and M.-A. Einarsrud, J. Non-Cryst. Solids 204, 228 (1996).
15. B.I. Lee and K.T. Chou, Mater. Lett. 14, 112 (1992).
16. G.W. Scherer, S. Hæreid, E. Nilsen, M.-A. Einarsrud, J. Non-Cryst. Solids 202, 42 (1996)
17. D.M. Smith, G.W. Scherer and J.M. Anderson, J. Non-Cryst. Solids 188, 191 (1995).
18. G.W. Scherer, D.M. Smith and D. Stein, J. Non-Cryst. Solids 186, 309 (1995).
19. F. Chaput, B. Dunn, P. Fuqua and K. Salloux, J. Non-Cryst. Solids 188, 11 (1995).
20. W. Dong and B. Dunn, submitted for publication.
21. Handbook of Chemistry and Physics vol. 74, ed. D.R. Lide, CRC Press (1993).
22. L.A. Girifalco and R.J. Good, J. Phys. Chem. 61, 904 (1957).
23. R.J. Good, L.A. Girifalco and G. Kraus, J. Phys. Chem. 62, 1418 (1958).
24. R.J. Good and L.A. Girifalco, J. Phys. Chem. 64, 561 (1960).
25. R.J. Good, J. Colloid and Interfacial Sci. 59, 398 (1976).
26. Y. Kano and S. Akiyama, Polymer 34, 1535 (1993).
27. C. J. Brinker and G. W. Scherer, Sol-Gel Science, Academic Press, San Diego (1990)
28. J.M. Miller, B. Dunn, J.S. Valentine and J.I. Zink, J. Non-Cryst. Solids 202, 279 (1996)

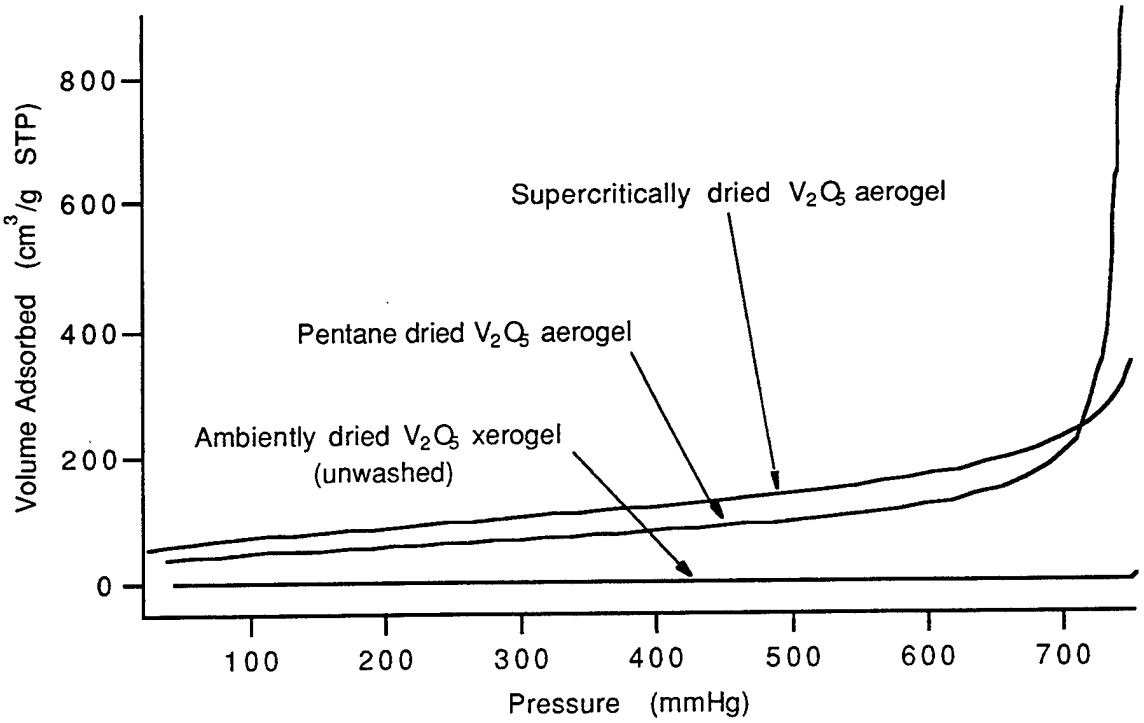

FIG. 1.
Nitrogen gas adsorption isotherms for vanadium oxide gel BET samples of ambiently dried xerogel, ambiently dried aerogel from pentane, and supercritically dried aerogel.